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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> <b>C08J 3/12, 3/24 // A61L 15/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 93/17066</b> <b>(43) International Publication Date:</b> 2 September 1993 (02.09.93)
<b>(21) International Application Number:</b> PCT/GB93/00357 <b>(22) International Filing Date:</b> 19 February 1993 (19.02.93)  <b>(30) Priority data:</b> 9203594.8                      20 February 1992 (20.02.92)    GB  <b>(60) Parent Application or Grant</b> <b>(63) Related by Continuation</b> US    857,502 (CIP) Filed on    25 March 1992 (25.03.92)  <b>(71) Applicant (for all designated States except US):</b> ALLIED COLLOIDS LIMITED [GB/GB]; P.O. Box 38, Low Moor, Bradford, West Yorkshire BD12 0JZ (GB).		<b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only) :</b> JOHNSON, Ian, Michael [GB/GB]; 69 Brow Lane, Shelf, Halifax, West York- shire HX3 7QL (GB).  <b>(74) Agent:</b> LAWRENCE, Peter, Robin, Broughton; Gill Jen- nings & Every, Broadgate House, 7 Eldon Street, Lon- don EC2M 7LH (GB).  <b>(81) Designated States:</b> AT, AU, BB, BG, BR, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI pa- tent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> ABSORBENT POLYMERS AND THEIR PRODUCTION  <b>(57) Abstract</b>  Absorbent particles consisting essentially of zones of polymeric material interconnected by linkages through an effective agglomerating amount of silica or silicate can be made by forming a gel mass by mixing particles of polymeric material with water and an effective agglomerating amount of a silica or silicate, and drying and comminuting the gel mass.		

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### Absorbent Polymers and their Production

This invention relates to aggregates of water swellable polymeric material.

We describe in, for instance, EP-A-401044 processes of  
5 making water insoluble, water swellable, particulate  
polymeric material from dry particles of water swellable  
polymer derived from water soluble ethylenically  
unsaturated material, wherein the process comprises forming  
a gel mass by absorbing aqueous solution of cross linking  
10 agent into the dry particles, causing cross linking of the  
polymer in the gel mass by reaction between the cross  
linking agent and pendant groups in the polymer, and drying  
and comminuting the gel mass. We also describe water  
insoluble, water swellable, particulate polymeric materials  
15 formed from ethylenically unsaturated material wherein the  
polymeric material has a polymer structure that is formed  
of zones in which the polymer is substantially free of  
cross links between pendant groups in the polymer and the  
zones are interconnected by cross links through pendant  
20 groups in the polymer. We describe that a polyvalent  
metal compound such as a compound of aluminium can be  
suitable for causing the cross linking between the polymer  
particles, and this will lead to ionic cross linking. A  
suitable material for this purpose is aluminium sulphate or  
25 other polyvalent metal compound salt.

We also describe that the cross linking compound is  
preferably one that leads to covalent cross linking and  
various hydroxy-containing and silane compounds are  
described for this purpose.

30 We describe that the technique is particularly  
valuable because it is capable of converting polymer fines  
into useful, coarser products, and that absorbent particles  
obtained in that invention, especially when the starting  
particles are cross linked sodium acrylate or similar  
35 particles, have particularly suitable properties when high  
gel capacity and high rate of absorption are required.

Although these processes are very successful for many purposes, it is sometimes found that the resulting aggregates crack or disintegrate during transport or use. It would be desirable to find a way of conducting the process, and producing products, that have satisfactorily low friability and advantageous properties from the point of view of total absorption and rate of absorption, for instance in diapers.

In the invention, an absorbent product comprises water swellable, particulate aggregates which consist essentially of polymeric material derived from ethylenically unsaturated material and which each comprise zones of the polymeric material interconnected by linkages through an effective agglomerating amount of silica or silicate.

A process according to the invention for making water swellable, particulate aggregates from particles of a water swellable polymeric material derived from water soluble ethylenically unsaturated polymer comprises forming a gel mass by mixing the particles of polymeric material with water and an effective agglomerating amount of a silica or a silicate, and drying and comminuting the gel mass.

The mixing conditions must be such as to convert the mixture of polymer particles, water and silica or silicate to a gel mass, and if there is any tendency for the particles to remain separate it may be desirable to increase the force of mixing. For instance the gel mass may be formed in an extruder used for the comminution.

In the invention, a mixture is formed of the polymer particles (generally in dry form), the silica or silicate, and water. The silica may be present as a suspension in water and the silicate may be present as a suspension or a solution in water, in which event the mixing stage can be conducted merely by mixing the polymer particles with the resultant aqueous suspension or solution.

Preferably, however, dry particulate silica or silicate is mixed with the polymer particles generally while they are still wholly or substantially dry, and

additional water is then mixed with the mixture to form the gel mass.

The preferred technique comprises dry mixing the polymer particles with dry silica particles, and then  
5 mixing the resultant mixture with water to form the gel mass.

The water that is used for mixing with the polymer particles may be a carrier for the silica or silicate. When, as is preferred, the polymer contains pendant groups  
10 (e.g. carboxylic groups) the water may also contain cross linking agent that will cross link between such groups. Suitable cross linking agents are described in EP 401044, such as any of the hydroxy or epoxy or silane compounds mentioned therein as cross linking agents.

15 The silica is preferably a fumed or precipitated silica and so will have very large surface area when dispersed in water, for instance 50 to 1000 g/m<sup>2</sup> and usually 100 to 750 g/m<sup>2</sup>. Preferably the surface area is above 100 or 150 g/m<sup>2</sup>, preferably above 200 g/m<sup>2</sup>. The  
20 particle size of the individual particles is generally below 30µm and typically in the range 0.1 to 10µm, often below 5µm, for instance 1 to 5µm. The silica is often supplied as aggregates, e.g. having a size of 10 to 100µm.

Instead of using fumed silica or precipitated silica,  
25 insoluble silicates can be used although they are usually less effective. The silicate is preferably silicic acid or a swelling clay, colloquially known as bentonite, which in practice is normally a smectite clay. If it is particulate, it should have small particle size and large  
30 surface area, e.g. as described above.

Colloidal or true solutions of silicates or silicic acid may be used instead of suspensions of insoluble silicates, but again they are usually less effective than fumed or precipitated silica.

35 Sufficient water must be applied to convert the starting polymer fines to an aqueous gel mass and the actual amount in any particular process will depend on the

moisture content of the polymer fines and the nature of the silica or silicate. For instance when, as is preferred, the silica is capable of absorbing significant amounts of water it is necessary to include sufficient water to allow  
5 for this absorption and for conversion of the particles to a gel mass. The total amount of water typically ranges from 25 to 300% based on the dry weight of polymer particles, with the higher amounts of water (e.g., above 150%) being preferred when water absorbent silica is  
10 incorporated. As explained in EP 401044, the extent of cross linking of the polymer particles influences the amount of water that is optimum.

The amount of silica or silicate must be sufficient to provide sufficient linkages between adjacent starting  
15 polymer particles in each aggregate such that the dry aggregates do not disintegrate to any significant extent when they absorb urine or other liquid. If too much is used, it may act as a release or barrier coating and prevent linkages being formed. If too little is used, it  
20 may not permit adequate linkages to be formed. The optimum depends on the material but is typically from 1 to 20% by weight based on the dry weight of polymer particles, with best results generally being obtained with amounts in the range about 3 or 5 to about 15%. However higher amounts,  
25 e.g., up to 25% or even more, may be appropriate in some instances especially when using a coarser or less effective material than fumed or precipitated silica.

The polymer particles that are aggregated in the invention can be water soluble polymer particles or,  
30 preferably, water swellable but water insoluble polymer particles. The aggregates are preferably water insoluble.

The dry particles that are used to form the gel mass preferably have a substantial proportion of fine particles in them. Generally at least 30%, and often at least 50%,  
35 may be fines, for instance below 200 $\mu$ m and usually below 150 $\mu$ m, preferably below 100 $\mu$ m. Particles below 50 $\mu$ m can cause particularly serious dusting problems and so the



invention is of particular value when applied to a fraction having at least 50%, and sometimes at least 90% by weight below 50 $\mu$ m.

5 The initial particles can be a fraction sieved from a product, in which event at least 90% of the particles will generally be below 200 and usually below 150 $\mu$ m, usually below 100 $\mu$ m.

10 The invention is, however, also of value for upgrading the quality of a particulate product that does contain particles of a satisfactory size above 200 $\mu$ m but also contains an unacceptably large proportion of fines. Thus the dry particulate product that is formed into the gel mass can be a product which is 0 to 70% by weight, often 0 to 50% by weight, above a chosen particle size and 30 to 15 100%, often 50 to 100% by weight below that particle size, generally 200 $\mu$ m or 150 $\mu$ m, more preferably 100 $\mu$ m.

20 The dry particles may have been made by reverse phase bead polymerisation, generally followed by sieving to produce a fines fraction for use in the invention, but more usually is made by a process comprising drying and comminution of larger particles. These larger particles may have been made by reverse phase bead polymerisation but, more usually, are made by comminution of gel made by bulk gel polymerisation.

25 The polymer in these particles can be linear but is generally a cross linked polymer. Usually it is a polymer formed from water soluble ethylenically unsaturated material comprising polyethylenically unsaturated cross linking agent with the result that the polymer is cross 30 linked in the backbone of the polymer. The water soluble ethylenically unsaturated material may be a single water soluble ethylenically unsaturated monomer or may be a water soluble blend of ethylenically unsaturated monomers.

35 The ethylenically unsaturated material can be non-ionic, anionic or cationic. If it is ionic, it can be a blend of non-ionic and ionic monomers, the amount of non-

ionic monomer often being 0 to 90%, and usually 0 to 70%, by weight of the blend.

The preferred ethylenically unsaturated material is generally anionic and may be formed from anionic monomer  
5 alone or a blend of anionic and non-ionic monomers. Although sulphonic monomers (e.g., allyl sulphonate or 2-acrylamido-2-methyl propane sulphonate) can form part of the anionic monomer, it is generally preferred that the ethylenically unsaturated material should comprise  
10 carboxylic monomer, for instance methacrylic acid, maleic acid, itaconic acid, crotonic acid or, preferably acrylic acid.

Suitable non-ionic monomers include vinyl pyrrolidone, methacrylamide or, preferably, acrylamide.

15 Suitable cationic monomers include dialkylaminoalkyl (meth) -acrylamides and -acrylates, usually as acid addition or quaternary salts. Examples are dimethylaminoethyl (meth) acrylates and dimethylaminopropyl (meth) acrylamides.

20 Preferred polymers are formed from 10 to 100%, often 30 to 100%, acrylic acid with the balance being acrylamide. The acrylic acid can be entirely in the form of free acid but, provided this does not interfere with the cross linking reaction, at least 50% and usually at least 75% of  
25 the acid groups are present in the form of sodium or other alkali metal or other water soluble salt.

The dry particles will often have conventional dryness as a result of drying followed by exposure to the ambient atmosphere, for instance below 15% moisture, and so the  
30 process can be applied to the treatment of previously made product. However the process of the invention can also be conducted as part of the overall production process starting with polymerisation of the monomer or monomer blend and then the dry particles do not have to be dried  
35 fully before they are rewetted and can, instead, still be slightly moist, for instance having a moisture content up to 20 or 25%. The must however be sufficiently dry that

they behave as fully dried particles rather than as sticky particles.

The aggregates are particulate and generally have a particle size of at least 90% by weight between 100 and 1000 $\mu$ m. They generally have a gel capacity of at least 20 (and preferably at least 50) grams deionised water per gram aggregate.

The absorbent products of the invention can be used as a replacement for conventional absorbent polymeric particles, e.g. in dewatering of mineral slurries or in absorbent articles such as diapers or sanitary napkins.

#### Example 1

Fines (generally having a size in the range 3 to 50 $\mu$ m) of cross linked sodium polyacrylate are dry blended with particulate fumed silica having a particle size below 4 $\mu$ m and the mixture is then sprayed with sufficient water to convert the mixture to a substantially homogeneous and sticky gel. When the amount of silica is 5%, an appropriate amount of water is 35g per 50g fines, but when the amount of silica is 15% an appropriate amount of water is 105g.

In each instance, the resultant gel is extruded, comminuted and dried, for instance in a fluid bed dryer, in a manner that is conventional for drying polymer gel.

The resultant product has very high absorbency and high gel strength both when dry and when swollen. For instance the gel strength in one example was 47,000 at a torque of 100,000 and an amplitude of 0.01A, compared to a gel strength of 36,000 when the silica was omitted and the water contained 0.1% ethylene glycol diglycidyl ether, as in EP 401044.

#### Example 2

The process of Example 1 is repeated except that 1% of that ether is incorporated in the water that is used for bonding the polymer-silica mixture. The gel strength increases from 47,000 to 75,000. Further increase is

obtainable when the ether is replaced by the silane cross linking agent used in the examples in EP 401044.

Example 3

5        In an alternative process, instead of dry mixing the  
silica with the polymer and then adding water, 47.5g  
polymer fines are mixed with a suspension of 2.5g silica in  
25g water. The mix is comminuted and dried as in Example  
1. This gives slightly lower gel strength and absorption  
10       are still satisfactory.

CLAIMS

1. A process for making water swellable particulate aggregates from particles of water swellable polymeric material derived from water soluble ethylenically unsaturated polymer comprising forming a gel mass by mixing the particles with water and drying and comminuting the gel mass, characterised in that the water includes an effective agglomerating amount of a silica or silicate.
2. A process according to claim 1 in which the water includes an effective agglomerating amount of a fumed or precipitated silica.
3. A process according to any preceding claim comprising forming a substantially dry mix of the polymer particles and the silica or silicate and then mixing the water with this mix.
4. A process according to any preceding claim comprising dry mixing dry fumed or precipitated silica with the polymer particles while substantially dry and then mixing the resultant mixture with water to form the gel mass.
5. A process according to any preceding claim in which the polymer includes pendant groups and the water contains cross linking agent that will cross link between the pendant groups.
6. A process according to any preceding claim in which the silica or silicate provides a surface area of above  $150\text{g/m}^2$ , the amount of silica or silicate is from 1 to 20% by weight based on the dry weight of polymer and the amount of water that is added to form the gel mass is from 25 to 300% by weight based on the dry weight of polymer.
7. A process according to any preceding claim in which the aggregates are water insoluble water swellable aggregates and are formed from water insoluble water swellable polymer particles.
8. A process according to claim 7 in which the water swellable polymer particles are formed of a cross linked polymer derived from 10 to 100% acrylic acid and 90 to 0% acrylamide.

9. A process according to any preceding claim comprising blending cross linked sodium polyacrylate particles having a size range mainly 3 to 50 $\mu$ m with fumed or precipitated silica and the resultant dry mix is mixed with water to  
5 form a substantially homogenous and sticky gel, and this gel is comminuted and dried.

10. An absorbent product comprising water swellable, particulate aggregates which consist essentially of polymeric material derived from ethylenically unsaturated  
10 material and which each comprise zones of the polymeric material interconnected by linkages through an effective agglomerating amount of silica or silicate.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 93/00357

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.C1. 5 C08J3/12; C08J3/24; //A61L15/00		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.C1. 5	C08J ; A61L	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	EP,A,0 450 922 (NIPPON SHOKUBAI KAGAKU KOGYO CO. LTD.) 9 October 1991 see claims 1,20,27 see page 3, line 42 - line 50 see page 7, line 26 - line 53 see page 8, line 41 - line 51 see examples 3,8; table 1 ---	1,3,5-8, 10
X	DATABASE WPIL Derwent Publications Ltd., London, GB; AN 89-353795[48] & JP,A,1 266 139 (KUNIMINE KOGYO KK) 24 January 1989 see abstract --- -/--	1,3,5,7, 8,10
<p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search 24 MAY 1993		Date of Mailing of this International Search Report 28. 05. 93
International Searching Authority EUROPEAN PATENT OFFICE		Signature of Authorized Officer NIAOUNAKIS M.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP,A,0 413 592 (ALLIED COLLOIDS LTD) 20 February 1991 see claims 1,4-7,9 see page 4, line 18 - line 22 see page 3, line 7 - line 11 -----	1



**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

**GB 9300357  
SA 70653**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0450922	09-10-91	AU-A- 7389291	03-10-91
		CN-A- 1056504	27-11-91
		JP-A- 4214736	05-08-92
EP-A-0413592	20-02-91	AU-A- 6101290	21-02-91
		AU-A- 6101790	21-02-91
		EP-A- 0413603	20-02-91
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		US-A- 5100467	31-03-92

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